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USE OF FERRIC SALT SOLUTIONS AS LEACHING AGENTS OF Co, Ni, Cu, Fe, AND Mn FROM METALLIC ALLOYS OF SPENT LITHIUM-ION BATTERIES AND SEPARATION OF IRON FROM THE LEACHING SOLUTION

T.T. Tran, M.S. Lee *

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam, Korea

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Abstract

Smelting reduction of spent lithium-ion batteries (LIBs) results in metallic alloys containing Co, Ni, Cu, Fe, and Mn. In order to recover the valuable metals contained in the metallic alloys, they need to be dissolved. In this work, the mixture of $Fe_2(SO_4)_3$ *and* $FeSO_4$*, single* $Fe_2(SO_4)$ *and* $FeCl_3$ *solutions were used as leaching agents and the effects of parameters such as ferric salt concentration, reaction temperature and time, and pulp density on the leaching of the metals were studied. The difference in the leaching percentage of the metals due to the type of the ferric solutions was insignificant. In these leaching systems, ferric and hydrogen ions act as oxidants and sulfate/bisulfate and chloride anions act as ligands. Optimal conditions for the complete leaching of metals by single ferric solutions were 0.35 mol/L* $Fe_2(SO_4)_3$ *or 0.7 mol/L* $FeCl_3$ *at 12.5 g/L pulp density for 60 min at 22°C. The addition of* H_2O_2 *to the leaching solution for the oxidation of Fe(II) to Fe(III) enhanced the selective extraction of iron over Co(II), Ni(II), Cu(II), Mn(II), and Si(IV) by D2EHPA. Stripping of iron from the loaded D2EHPA with aqua regia resulted in a pure iron solution. Compared to HCl and* H_2SO_4 *solutions, the use of single ferric solution showed some advantages such as fast reaction kinetics at 22°C and the reduction in the dosage of acids and oxidants.*

Keywords: *Hydrometallurgy; Leaching; Recovery; Separation; Lithium-ion batteries*

1. Introduction

The rapid growth of electric vehicles (EVs) has increased the usage of lithium-ion batteries (LIBs) in recent years [1]. In 2021, global EV market was 4,093 thousand units and it is forecasted to hit 34,756 thousand units by 2030 at a compound annual growth rate (CAGR) of 26.8% [2]. In addition, the application of LIBs to stationary energy storage together with the increasing demand for LIBs in electronic devices has also contributed to the significant increase in LIBs consumption [3]. As a result, a large amount of LIBs after the end of life are discarded and less than 5% of them is recycled at present [4]. It is estimated that by 2030 the number of spent LIBs over worldwide will reach about 2 million metric tons per year [5]. Proper handling of the spent LIBs would lessen environmental impacts by the heavy metals (e.g. Co, Ni, Cu, Al, Fe, etc.), fluorine, and organic matters [6]. With the extending production of LIBs, the demand for component materials, especially strategic metals like Co, Ni, and Li has rapidly increased and will continually rise in the future [7, 8]. Therefore, it is necessary to increase the recycling rate of spent LIBs, which could ensure sustainable LIBs production in the future and reduce environmental issues.

The recovery of valuable metals like Co, Ni, Cu, and Li from spent LIBs has been reported in many processes including pyro-, hydro-, and bio-metallurgy or the pyro/hydrometallurgical combination [9-11]. Among these processes, the combination of pyro- and hydro-metallurgy is considered to be more effective than others in the recovery of Co, Ni, and Cu [12]. Initially, spent LIBs without any pretreatment undergoes gradual heating treatment at various high temperatures consisting of preheating (<300°C) for the evaporation of electrolyte, pyrolysis (>700°C) for the removal of plastics, and smelting reduction by which metal oxides are reduced to metallic alloys (e.g. Co, Ni, and Cu) and base metals are distributed into slag and dust [11, 13]. Afterward, hydrometallurgical processes consisting of leaching and separation steps (e.g. solvent extraction, precipitation, and ion exchange) would be employed for the recovery of metals from the metallic alloys and dust [14-16]. The separation of the dissolved metal ions from the leaching solution of the metallic

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Corresponding author: mslee@mokpo.ac.kr

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alloys is rather complicated due to the presence of various metal components (e.g. Co, Ni, Cu, Fe, and Mn) as well as their high concentrations in the leaching solutions. Meanwhile, few works have been reported for the recovery of Li from the slag and dust. Therefore, further studies are necessary for the recovery of metals from the spent LIBs after the heating treatment processes.

During smelting reduction of spent LIBs, metallic alloys containing Co, Ni, Cu, Mn, Fe, and Si are produced. In our previous works, hydrometallurgical processes for the recovery of these metal ions from the metallic alloys were reported. Those processes consisted of leaching with either HCl or H_2SO_4 solution in the presence of oxidizing agent followed by separation steps such as solvent extraction and oxidative precipitation [17, 18]. However, the use of oxidizing agents at high concentration (10% (v/v) H_2O_2) in strong acid medium (2.0 mol/L acids) was required in the proposed processes. In aqueous solution, ferric ion can act as an oxidizing agent owing to its high standard reduction potential, $E^o_{Fe(III)/Fe(II)}$ = 0.77 V. As an alternative for HCl and H_2SO_4 containing H_2O_2, ferric sulfate and ferric chloride solutions were employed in this work as lixiviants for the leaching of metals from the metallic alloys. Since the metallic alloys contain a small amount of iron, the use of ferric sulfate has some advantages in the process economics. Optimal conditions for the leaching of metals from the alloys such as concentration of Fe(III), reaction time and temperature, and pulp density were investigated. The effect of Fe(III) in sulfate and chloride mediums on the leaching efficiency of metals was compared. Studies for the selective removal of iron over other metal ions from the leaching solutions was also investigated.

2. Experimental

2.1. Reagents and Chemicals

Iron(III) solutions were prepared by dissolving iron(III) sulfate n-hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$, Kanto Chemical Co. INC, Japan, 60-80%), iron(II) sulfate hexahydrate ($FeSO_4 \cdot 6H_2O$, Junsei Chemical Co. Ltd., 99%) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Showa Chemicals INC., Japan, 97.0%) in distilled water to the desired concentrations. Concentrated acid solutions like hydrochloric acid (HCl, Daejung Chemical & Metals Co., Korea, 35%) and nitric acid (HNO_3, Daejung Chemical & Metals Co., Korea, 60%) were employed without any purification. Hydrogen peroxide (H_2O_2, Daejung Chemical & Metals Co., Korea, 30%) was employed to oxidize Fe(II) to Fe(III).

Organic extractant, di-(2-ethylhexyl) phosphoric acid (D2EHPA, Cytec Industries Inc., USA, 95%) was used without any purification. Commercial grade kerosene (Daejung Chemical & Metals Co., Korea, >90 %,) was used as a diluent.

2.2. Characteristics of metallic alloys

The metallic alloys from the smelting reduction of spent LIBs were supplied by a Korean company. Metallic alloy powders with less than 100 *m*m particle size were employed in the experiments. X-ray diffractometer measurement (XRD, X'Pert-PRO, the Netherlands) in the previous study confirmed that metallic alloy powders consisted of Co, Ni, Cu, Mn, and Fe [17]. Chemical composition of the powders is displayed in Table 1, which was obtained by completely dissolving a certain amount of powders with aqua regia and then the concentration of the metal ions in the resulting solution was measured by Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany).

2.3. Leaching and solvent extraction procedure

2.3.1. Leaching procedure

Certain amount of the alloy powders was added into a 250 cm^3 three-neck round bottom flask containing the desired concentration of Fe(III) solution. The weight ratio of the alloys to the leaching solution (pulp density) was fixed at 20 g/L, except for experiments on the effect of pulp density. Leaching experiments were performed at the desired reaction temperature and time, while stirring speed was fixed 500 rpm. A magnetic stirrer (WiseStir MSH-20D, Daihan Scienctific Co., Korea) was employed to control reaction time, temperature, and stirring speed. The concentration of metal ions in the leaching solution was measured by ICP-OES. The leaching percentage of metals from the alloys was calculated as: Leaching efficiency (%) = m_{aq}/m_i x 100 %, where m_i is the mass of a metal in the alloys before leaching and m_{aq} is mass of the metal in the aqueous solution after leaching, which was obtained from the ICP-OES measurement.

2.3.2. Solvent extraction procedure

The mixture of equal volume of aqueous and organic solutions (each 20 mL) in a screwed cap bottle was shaken by a Burrell wrist action shaker

Table 1. *Chemical composition of the metallic alloy powders resulted from the smelting reduction of spent LIBs*

Elements	Co	Ni	Cu	Mn	Fe	Si	O
Weight percentage, wt.%	12.9	61.99	22.33	1.58	0.50	0.33	0.37

(model 75, USA) at ambient temperature (22 ± 1°C) for 30 min. After the required time, the shaken solutions were stood in a glass separatory funnel for phase separation. The concentration of metal ions in the aqueous phase was determined by ICP-OES. Extraction percentage (%E) was calculated by the mass ratio of a metal in organic phase (m_{org}) after extraction to that in the aqueous phase (m_{aq}) before extraction: %E = m_{org}/m_{aq} x 100%. Stripping percentage of a metal was calculated as: % stripping = m^{*aq}/m_{org} x 100%, where m^*_{aq} is the mass of metal in aqueous phase after stripping.

Concentration of hydrogen ions in the aqueous solutions was measured by titration methods or pH meter (Orion Star, model A221, USA). It was assumed that the change in the volume of the two phases during solvent extraction experiments was negligible. Experiments were done twice and the errors were within ±5%.

3. Results and discussion

3.1. Leaching of metals from the alloys using the mixture of $Fe_2(SO_4)_3$ and $FeSO_4$

In general, oxidizing agents are necessary to dissolve Cu due to its high reduction potential ($E^o_{Cu2+/Cu}$ = 0.34 V) (see Table 2). Since the reduction potential of ferric to ferrous ion is higher than that of Cu(II), the mixture of ferrous and ferric sulphate or chloride could dissolve Cu [19, 20]. Therefore, the mixture of $Fe_2(SO_4)_3$ and $FeSO_4$ was employed as a lixiviant for the leaching of metals from the alloys. The leaching of metals from the alloys by the mixed solutions is a redox reaction where the anodic and cathodic reactions can be represented as

$$M = M^{2+} + 2e\ ;\ \left(E^o_{M2+/M} = -1.18 \sim 0.34V\right) \tag{1}$$

$$Fe^{3+} + e = Fe^{2+}\ ;\ \left(E^o_{Fe3+/Fe2+} = 0.77V\right) \tag{2}$$

where M denotes Co, Ni, Mn, Fe, and Cu.

First, the total concentration of $Fe_2(SO_4)_3$ and $FeSO_4$ in the leaching solution was varied from 0.3 to 1.5 mol/L at unity molar ratio. Leaching experiments were carried out at 20 g/L pulp density for 180 min at 60°C. Fig. 1 shows that the leaching percentage of metals increased with rising the total concentration of iron ions in the leaching solution. Namely, Ni, Mn, and Fe were completely dissolved at the total concentration of 1.0 mol/L iron, whereas the leaching percentage of Co, Cu, and Si was only 69.6, 70.6, and 20.5% at this concentration, respectively.

Since the reduction potential of the mixture of ferric and ferrous ion depends on the concentration ratio of the two ions, the concentration ratio of $Fe_2(SO_4)_3$ to $FeSO_4$ in the leaching solution was varied from 0.25 to 4. In these experiments, the total concentration of iron was fixed at 1.0 mol/L. Leaching experiments were done at 20 g/L pulp density for 180 min at 60°C. As presented in Fig. 2, the leaching percentage of Ni, Mn, and Fe rose from 46.1, 66.6, and 68.7% to completeness, while that of Co and Cu increased from 36.1 and 34.7% to 76.5 and 83.7% with the concentration ratio of $Fe_2(SO_4)_3$ to $FeSO_4$ and that of Si was fluctuated from 15.1 to 22.5%.

3.2. Leaching of metals from the alloys using single $Fe_2(SO_4)_3$ solution

3.2.1. Effect of $Fe_2(SO_4)_3$ concentration

The results in previous section indicate that higher concentration ratio of ferric to ferrous ion is

Table 2. *Standard reduction potentials (E^o) of some reactions at 25°C [21, 22]*

Reduction half-reaction	E^o, Volt
$Mn^{2+}_{(aq)} + 2e = Mn_{(s)}$	-1.18
$Fe^{2+}_{(aq)} + 2e = Fe_{(s)}$	-0.40
$Co^{2+}_{(aq)} + 2e = Co_{(s)}$	-0.28
$Ni^{2+}_{(aq)} + 2e = Ni_{(s)}$	-0.26
$Fe^{3+}_{(aq)} + 3e = Fe_{(s)}$	-0.06
$Cu^{2+}_{(aq)} + e = Cu^{+}_{(aq)}$	+0.15
$Cu^{2+}_{(aq)} + 2e = Cu_{(s)}$	+0.34
$Cu^{+}_{(aq)} + e = Cu_{(s)}$	+0.52
$Fe^{3+}_{(aq)} + e = Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 4H^{+}_{(aq)} + 4e = 2H_2O_{(l)}$	+1.23
$Mn^{3+}_{(aq)} + e = Mn^{2+}_{(aq)}$; at pH =1	+1.56
$H_2O_{2(aq)} + 2H^{+}_{(aq)} + 2e = 2H_2O_{(l)}$	+1.78

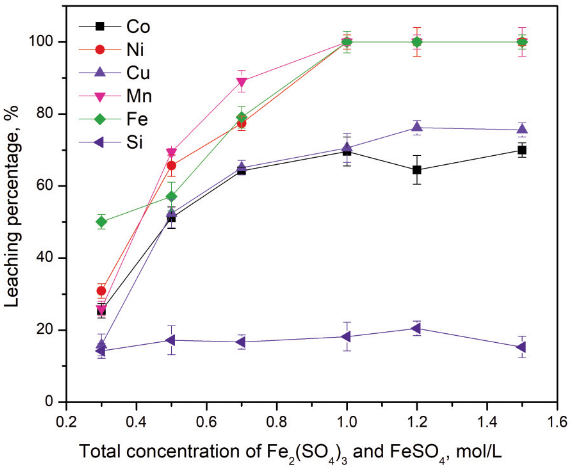

Figure 1. *Effect of the total concentration of $Fe_2(SO_4)_3$ and $FeSO_4$ in the leaching solution on the leaching of metals from the alloys. (The concentration ratio of $Fe_2(SO_4)_3$ to $FeSO_4$ was unity, 20 g/L pulp density for 180 min at 60 °C)*

favourable to the leaching of the metals from the alloys. Since the reduction potential of ferrous ion is much smaller than that of ferric ion, iron would be dissolved as ferrous ion in the leaching. Therefore, it can be said that single $Fe_2(SO_4)_3$ solution can be employed as a leaching agent for our purpose because the dissolution of iron as ferrous ion leads to the reduction potential which is required to dissolve Cu.

The concentration of $Fe_2(SO_4)_3$ in the leaching solutions was varied from 0.15 to 0.75 mol/L. Experiments were carried out at 60ºC for 180 min with 20 g/L pulp density. In Fig. 3, Ni, Mn, and Fe were quantitatively dissolved with 0.35 mol/L $Fe_2(SO_4)_3$, whereas the leaching percentage of Co, Cu, and Si reached 87.2, 90.5, and 18.6% in these concentration ranges, respectively. The leaching efficiency of metals from the alloys by single $Fe_2(SO_4)_3$ solutions was ascribed to the oxidizing power of ferric ions together with the complex formation between the dissolved ions and sulfate/bisulfate ions. It is noticeable that there was a slight decrease in the leaching percentage of Co from 87.2 to 84.6% and that of Cu from 90.53 to 78.2% when $Fe_2(SO_4)_3$ concentration was higher than 1.0 mol/L. Table 3 represents the pH value of the solution with the concentration of $Fe_2(SO_4)_3$ before and after leaching. It is seen in Table 3 that the change in the concentration of hydrogen ion owing to the leaching reaction is proportional to the concentration of $Fe_2(SO_4)_3$. Since the leaching percentage of the metals increased with $Fe_2(SO_4)_3$ concentration, more hydrogen ions are involved in dissolving the metals except Cu, which agrees well with the data reported in Table 3. Since ferric ion has a high charge density, it has a strong tendency to be hydrolysed (Eq**s**. (3)-(4)) [23, 24]. Therefore, the acidity of the $Fe_2(SO_4)_3$ solution would be stronger with its concentration and the hydrogen ions resulted from the hydrolysis of Fe(III) participate in the leaching of metals from the alloys. The hydrolysis reactions of $Fe_2(SO_4)_3$ in the aqueous solution can be written as

$$Fe_2\left(SO_4\right)_3 = 2Fe^{3+} + 3SO_4^{\,2-} \tag{3}$$

$$Fe^{3+} + xH_2O = \left[Fe\left(OH\right)_x\right]^{3-x} + xH^+ \tag{4}$$

Comparison between Fig. 2 and 3 indicates that there was a small difference in the leaching percentage of metals between single $Fe_2(SO_4)_3$ solution and the mixture of $Fe_2(SO_4)_3$ and $FeSO_4$. Fig. 3 also shows that it is difficult to completely dissolve the metals by just increasing the concentration of $Fe_2(SO_4)_3$. The optimum concentration of $Fe_2(SO_4)_3$ in the leaching solution was selected to be 0.35 mol/L.

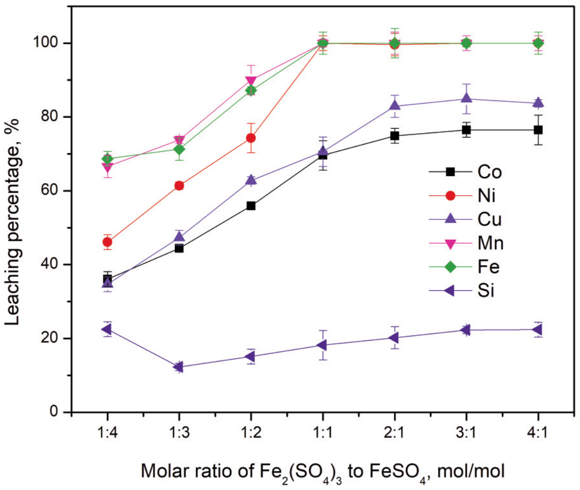

Figure 2. *Effect of molar ratio of $Fe_2(SO_4)_3$ to $FeSO_4$ on the leaching of metals from the alloys.(The total concentration of iron was 1.0 mol/L, 20 g/L pulp density, 60ºC for 180 min)*

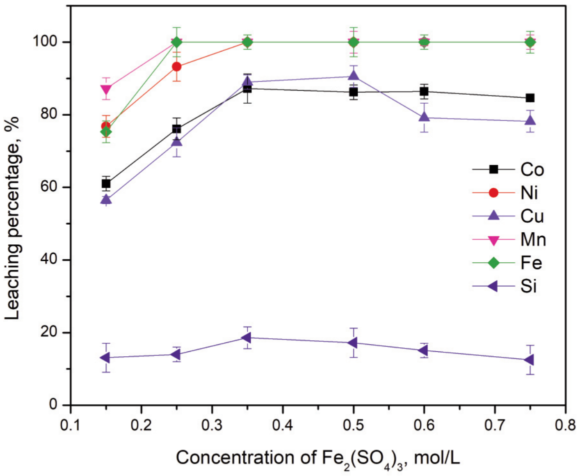

Figure 3. *Effect of $Fe_2(SO_4)_3$ concentration on the leaching of metals from the alloys.(20 g/L pulp density, 60ºC for 180 min)*

Table 3. *Variation in the initial and final pH of the solution with $Fe_2(SO_4)_3$ concentration*

Concentration of $Fe_2(SO_4)_3$, mol/L	0.15	0.25	0.35	0.50	0.60	0.75
Initial pH value,	1.17	0.93	0.75	0.51	0.35	0.15
Final pH value	1.96	1.53	1.14	0.76	0.54	0.27
Change in the concentration of hydrogen ion(Δ[H^+], mol/L)	0.06	0.09	0.11	0.15	0.16	0.17

3.2.2. Effect of reaction temperature

The effect of temperature on the leaching of metals from the alloys was investigated in the temperature range from 22 to 80°C. $Fe_2(SO_4)_3$ concentration in the leaching solution was fixed at 0.35 mol/L with 20 g/L pulp density for 180 min. Fig. 4 shows that Ni, Fe, and Mn were quantitatively leached from the alloy at the studied temperature range, while the leaching percentage of other metals slightly increased from 89.3 to 97.1% for Co, from 85.7 to 92.7% for Cu and 14.8 to 16.6% for Si. These results revealed that the effect of temperature on the leaching performance is not significant. Therefore, room temperature was selected for the leaching of metals from the alloys by single $Fe_2(SO_4)_3$ solution.

3.2.3. Effect of reaction time

To consider the effect of reaction time on the leaching efficiency of metals from the alloys, leaching time was varied from 30 to 360 min at 0.35 mol/L $Fe_2(SO_4)_3$, 20g/L pulp density at room temperature. In Fig. 5, Ni, Fe, and Mn were completely dissolved within 60 min, whereas the leaching percentage of other metals increased from 55.5 to 91.1% for Co, 56.3 % to 87.1% for Cu and from 13.9 to 17.7% for Si with the reaction time. These results indicated that the complete leaching of the metals from the alloys was difficult by just extending the reaction time. Therefore, the leaching reaction time of 60 min was considered to be the optimum condition for the leaching.

3.2.4. Effect of pulp density

To completely leach the metals from the alloys by single $Fe_2(SO_4)_3$ solution, pulp density was decreased from 20 g/L. Leaching experiments were carried out with 0.35 mol/L $Fe_2(SO_4)_3$ at room temperature for 60 min. As represented in Fig. 6, the leaching percentage of metals from the alloys significantly increased with a decrease in the pulp density and complete leaching of the metals was obtained at 12.5 g/L pulp density.

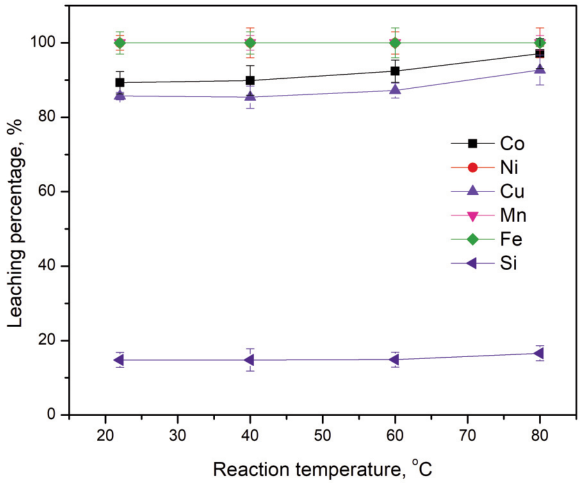

***Figure 4.** Effect of temperature on the leaching of metals from the alloys. (Leaching conditions: 0.35 mol/L $Fe_2(SO_4)_3$, 20g/L pulp density and 180 min)*

From the obtained results, optimum conditions for the complete leaching of metals from the alloys by single $Fe_2(SO_4)_3$ solution was 0.35 mol/L $Fe_2(SO_4)_3$, 12.5 g/L pulp density, 60 min reaction time, and room temperature. Under these optimum conditions, the concentration of the dissolved metal ions and Si(IV) in the leaching solution is displayed in Table 4 and the final pH (pH_f) of the leaching solution was 1.28.

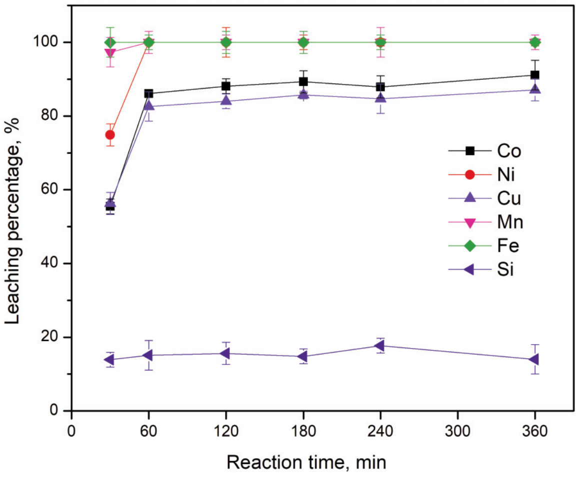

***Figure 5.** Effect of reaction time on the leaching of metals from the alloys. (Leaching conditions: 0.35 mol/L $Fe_2(SO_4)_3$, 20 g/L pulp density at room temperature)*

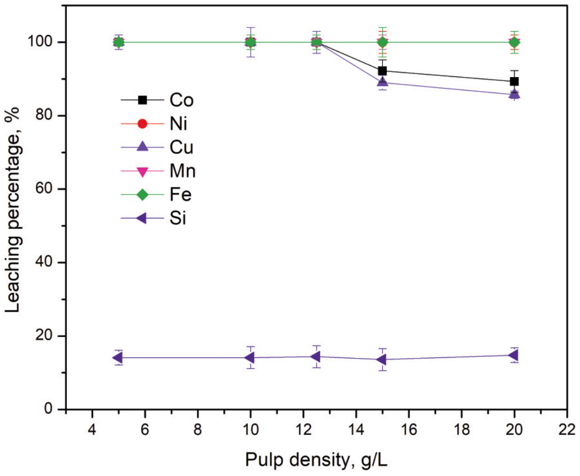

***Figure 6.** Effect of pulp density on the leaching of metals from the alloys. (Leaching conditions: 0.35 mol/L $Fe_2(SO_4)_3$, 60 min at room temperature)*

3.3. Leaching of metals from the alloys using single $FeCl_3$ solution

Single $FeCl_3$ solution was employed to investigate the leaching behavior of the metals from the alloys under the conditions of 0.7 mol/L $FeCl_3$, 20 g/L pulp density, and room temperature within 180 min. In these experiments, the concentration of $FeCl_3$ was controlled to be 0.7 mol/L, considering that the optimum concentration of $Fe_2(SO_4)_3$ was 0.35 mol/L. Our results confirmed that the difference in the leaching percentage of metals between single $FeCl_3$ and $Fe_2(SO_4)_3$ solution was less than 2.0%. Namely, Ni, Mn, and Fe were completely dissolved, while the leaching percentage of Co and Cu was 89.0 and 88.9% respectively. However, the leaching percentage of Si by $FeCl_3$ solution was 56.6% which was higher than that by $Fe_2(SO_4)_3$ solution (18.6%).

The optimum conditions of $Fe_2(SO_4)_3$ solution for the leaching of the metals from the alloys (0.35 mol/L $Fe_2(SO_4)_3$, 12.5 g/L pulp density for 60 min at room temperature) was also applied for $FeCl_3$ solution. Our data indicated that Co, Ni, Cu, Mn, and Fe were completely leached and the leaching percentage of Si was 47.7%. The concentrations of Co(II), Ni(II), Cu(II), Mn(II), and Si(IV) in the leaching solution are displayed in Table 4. Final pH of the solution after the leaching was 1.42. Our data clearly indicate that complete leaching of metals from the metallic alloys can be possible by using single either $Fe_2(SO_4)_3$ or $FeCl_3$ solutions.

Our data shows that ferric and hydrogen ions play a role as oxidants for the dissolution of Co, Ni, Mn, Fe, and Cu from the metallic alloys, whereas anions like sulfate/bisulfate or chloride are reacting as ligands to the dissolved metal ions [25, 26]. Considering the reduction potential of Cu(I) and Cu(II), Cu metal would be dissolved as Cu(II) not Cu(I) in our experimental conditions because the reduction potential of Cu(II) (E^o = 0.34V) (0.34V) is much lower than that of Cu(I) (E^o =0.52V) [27]. Therefore, the dissolved metal ions except iron exist as divalent ions, while iron exists as both ferrous and ferric and Si exists as silicate. Therefore, the leaching reactions of metals by ferric ion in our systems can be written as follows

$$M_{(s)} + 2Fe^{3+}_{(aq)} = M^{2+}_{(aq)} + 2Fe^{2+}_{(aq)} \tag{5}$$

$$M^{2+}_{(aq)} + nSO_4{}^{2-}_{(aq)} = M\left(SO_4\right)_n{}^{2-2n}_{(aq)} \tag{6}$$

$$M^{2+}_{(aq)} + nCl^{-}_{(aq)} = MCl_n{}^{2-n}_{(aq)} \tag{7}$$

Our previous studies showed that the complete leaching of metals from the alloys by acidic solutions required 2.0 mol/L HCl or H_2SO_4, 10% (v/v) H_2O_2 at 60°C with 150 or 240 min reaction time [17, 18]. Compared with the leaching of metals by acid solutions containing H_2O_2 as an oxidizing agent, either single $Fe_2(SO_4)_3$ or $FeCl_3$ solution showed some advantages in the recovery of metals such as: (1) the role of ferric salts as an oxidizing agent which would improve the process economics, (2) fast reaction kinetics, (3) low energy consumption due to leaching reactions at room temperatures, and (4) a decrease in the consumption of acids. Therefore, the separation of Co(II), Ni(II), Cu(II), Mn(II), Fe(III), and Fe(II) from the sulfate and chloride leaching solutions will be studied further.

3.4. Removal of iron from the leaching solutions

3.4.1. Solvent extraction of iron by D2EHPA

In our previous studies, the selective separation of Fe(III) over Co(II), Ni(II), Cu(II), and Mn(II) from the sulfate and chloride leaching solutions was obtained by solvent extraction with D2EHPA [17, 18]. Therefore, D2EHPA in kerosene was employed for the removal of Fe(II) and Fe(III) ions from the leaching solutions by ferric salt solutions. In the solvent extraction experiments, concentration of D2EHPA was varied from 0.5 to 2.0 mol/L. Fig. 7 shows that the extraction percentage of iron was only from 14.2 to 26.4% in the concentration range of D2EHPA. These results can be ascribed to the high concentration of Fe(II) in the leaching solution. In general, the extraction percentage of Fe(II) by D2EHPA was much lower than that of Fe(III) at the same acidity level. Therefore, oxidation of Fe(II) to Fe(III) is needed to increase the extraction efficiency of iron from the leaching solution. This can be accomplished by blowing oxygen or the addition of oxidizing agents like H_2O_2 to the leaching solution.

In this work, 20% (v/v) of H_2O_2 was first added to oxidize Fe(II) to Fe(III) and then solvent extraction with D2EHPA was done. As presented in Fig. 8, the extraction percentage of Fe(III) increased from 26.8 to 73.1 % as the concentration of D2EHPA increased from 0.5 to 2.0 mol/L, whereas other ions were not extracted at all. The decrease in pH value of the

Table 4. *Concentration of metal ions in the Fe(III) leaching solutions under the optimum leaching conditions (0.7 mol/L Fe(III), 12.5 g/L pulp density, 60 min at room temperature)*

Concentration of metal ions in the leachate	Co(II)	Ni(II)	Cu(II)	Total iron	Mn(II)	Si(IV)
$Fe_2(SO_4)_3$, mg/L	1644.7	7904.1	2825.8	40320.2	201.5	6.2
$FeCl_3$, mg/L	1643.0	7908.2	2820.1	40286.4	205.4	25.0

aqueous phase after the extraction was also observed from 1.42 to 0.54, which was ascribed to liberation of hydrogen ions from D2EHPA into the aqueous phase according to ion exchange mechanism. In the case of the $FeCl_3$ leaching solution, the extraction percentage of Fe(III) from the leaching solution after treated by H_2O_2 solution was 75.0%. These results showed that the difference in the extraction behavior of Fe(III) by D2EHPA between sulfate and chloride solution was negligible. The extraction reaction of Fe(III) ions from the sulfate and chloride solutions by D2EHPA can be written as [28-30]

$$Fe^{3+}{}_{(aq)} + 3H_2A_{2(org)} = FeA_3 \cdot 3HA_{(org)} + 3H^+{}_{(aq)} \quad (8)$$

$$Fe^{3+}{}_{(aq)} + Cl^-{}_{(aq)} + H_2A_{2(org)} = FeClA_2{}_{(org)} + 2H^+{}_{(aq)} \quad (9)$$

where H_2A_2 is dimeric form of D2EHPA.

To completely extract Fe(III) ions from the leaching solution, cross-current extraction with 2.0 mol/L D2EHPA at an O/A ratio of unity was performed. The obtained data showed that Fe(III) was completely extracted after three-stage cross-current extraction, while the extraction percentages of other metals was negligible. The extraction percentage of Fe(III) at each stage is shown in Fig. 9. The concentration of hydrogen ions after the complete extraction of Fe(III) was determined to be 0.5 mol/L. Similarly, the complete extraction of Fe(III) from the chloride leaching solution was also obtained by three stage cross-current extraction with 2.0 mol/L D2EHPA at an O/A ratio of unity.

Thus, after three stages of cross-current extraction with D2EHPA, Fe(III) ions from the leaching solution were selectively and completely extracted over others. To recover iron from the loaded D2EHPA, stripping experiments were done.

3.4.2. Stripping of Fe(III) from the loaded D2EHPA

When the concentration of Fe(III) in the loaded D2EHPA is high, it is difficult to completely strip Fe(III) from the loaded D2EHPA [31]. Although the stripping of Fe(III) from the loaded D2EHPA can be improved by using reducing agents such as SO_2, H_2SO_3 and Na_2SO_3, multi-stage stripping is required for the complete stripping of Fe(III) [27]. In our previous studies, the complete stripping of Fe(III)

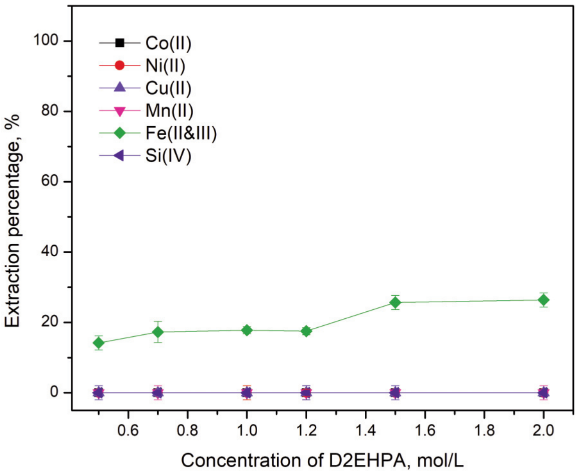

Figure 7. *Effect of D2EHPA concentration on the extraction of Fe(III) and Fe(II) from the sulfate leaching solution at an O/A ratio of unity*

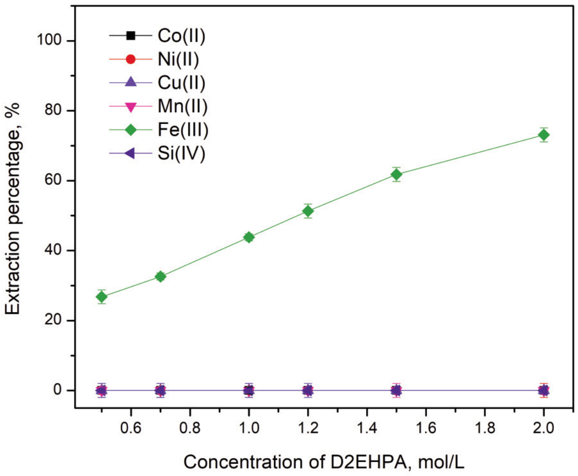

Figure 8. *Effect of D2EHPA concentration on the extraction percentage of Fe(III) from the sulfate leaching solution after oxidization with H_2O_2*

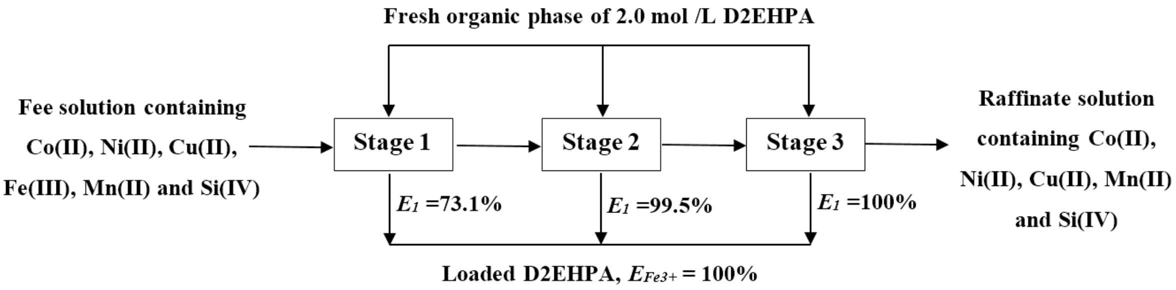

Fig. 9 *Cross-current extraction of Fe(III) from the sulfate leaching solution after the addition of H_2O_2 at an O/A ratio of unity*

from the loaded D2EHPA was obtained using aqua regia solution and the effect of aqua regia on the chemical structure of D2EHPA after the stripping was found to be insignificant [18]. Hence, in this work, aqua regia solution was employed for the stripping of Fe(III) from the loaded phase. Concentration of aqua regia was varied from 30 to 60 %(v/v). Fig. 10 displays that the stripping percentage of Fe(III) sulfate from the loaded D2EHPA increased from 50.4 to 84.0% with the concentration of aqua regia. Likewise, the stripping percentage of Fe(III) chloride from the loaded D2EHPA was 81.0% at 60% (v/v) aqua regia. In both cases, the complete stripping of Fe(III) from the loaded phase was obtained by two stages of cross-current stripping with 60%(v/v) aqua regia solution at an O/A ratio of unity. The purity of Fe(III) in the stripping solution was higher than 99.9%. The stripping reactions of Fe(III) from the loaded D2EHPA can be proposed as:

$$FeA_3 \cdot 3HA_{(org)} + 3H^+_{(aq)} + nCl^-_{(aq)} = FeCl_n^{(3-n)}{}_{(aq)} + 6HA_{(org)} \quad (10)$$

$$FeClA_{2\,(org)} + 2H^+_{(aq)} + (n-1)Cl^-_{(aq)} = FeCl_n^{(3-n)}{}_{(aq)} + 2HA_{(org)} \quad (11)$$

Thus, iron from the sulfate and chloride leaching solutions was selectively separated by extraction with D2EHPA and then stripping of iron by aqua regia. The concentration of Co(II), Ni(II), Cu(II), and Mn(II) in the iron free raffinate is presented in Table 5.

Table 5. *Concentration of metals in Fe(III) free sulfate rafinate after the three-stage cross current extraction with 0.5 mol/L D2EHPA at O/A =1*

Metal ions in the leachate	Co(II)	Ni(II)	Cu(II)	Mn(II)	Si(IV)
mg/L	1374.6	6580.5	2358.3	167.1	5.2

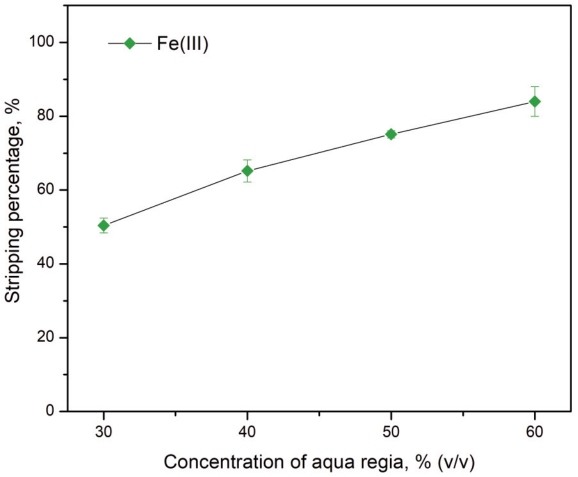

Figure 10. *Effect of aqua regia concentration on the stripping of Fe(III) from the loaded D2EHPA at an O/A ratio of unity*

The separation of Co(II), Ni(II), Cu(II), Mn(II), and Si(IV) from the sulfate and chloride raffinate can be accomplished by using selective extractants like Cyanex 301 or ALi-Cy301 for Cu(II), ALi-SCN for Co(II), and NaClO for the precipitation of Mn(II) as MnO_2 and then Ni(II) and Si(IV) would remain in the final filtrate [17, 18]. Ni(II) can be selectively recovered over Si(IV) from the filtrate by precipitation with $Na_2C_2O_4$ [32].

Table 6 summarizes the advantages and disadvantages of the leaching systems in the recovery of metals from the metallic alloys. Compared to either HCl or H_2SO_4 solution containing H_2O_2 as an oxidizing agent, single ferric sulfate or chloride solution shows better efficiency in metal recovery in terms of process economics and chemical dosage. Ferric solutions can completely dissolve metals with fast leaching kinetics, low energy consumption, and reduction in acid dosage, which can decrease the cost

Table 6. *Advantages and disadvantages in the recovery of metals from the metallic alloys of the reduction smelted spent LIBs in previous and present works*

	Previous works		This work
Process	HCl & H_2O_2 solution	H_2SO_4 & H_2O_2 solution	Ferric salt solutions
Leaching conditions	2.0 mol/L HCl, 5% (v/v) H_2O_2 with 30 g/L pulp density at 60°C for 150 min.	2.0 mol/L, 10% (v/v) H_2O_2 with 25 g/L pulp density at 60°C for 240 min.	0.35 mol/L $Fe_2(SO_4)_3$ or 0.7 mol $FeCl_3$ with 12.5 g/L pulp density for 60 min at room temperature.
Separation steps	(1) 0.5 mol/L D2EHPA for extraction of Fe(III) and stripping with 50% (v/v) aqua regia.	(1) 0.2 mol/L ALi-Cy301 for extraction of Cu(II) and stripping with 4.0 mol/L HNO_3.	(1) 2.0 mol/L D2EHPA for extraction of Fe(III) after treated with 20% (v/v) H_2O_2 for oxidizing Fe(II) to Fe(III) and stripping with 60%(v/v) aqua regia.

Table continues on next page

Continuation of the table from the previous page

	(2) 0.25 mol/L Cyanex301 for extraction of Cu(II) and stripping with 50% (v/v) aqua regia.	(2) 0.5 mol/L ALi-SCN for extraction of Co(II) and Fe(III) and stripping with 10%(v/v) NH_3 solution.	(2) Other metals such as Co(II), Ni(II), Cu(II), and Mn(II) can be recovered by using Cyanex031, ALi-SCN for the solvent extraction and NaClO for the precipitation of Mn(II) over Ni(II).
	(3) 0.25 mol/L ALi-SCN for extraction of Co(II) and stripping with 10%(v/v) NH_3 solution.	(3) 10% (v/v) NaClO at pH 3 for precipitation of Mn(II).	
	(4) 10% (v/v) NaClO at pH 3 for precipitation of Mn(II).	(4) Ni in the filtrate	
	(5) Ni in the filtrate		
Advantages	• Complete leaching of metals.		• Complete leaching of metals
	• Metal ions were sequentially and effectively recovered with high purity.		• Low chemical consumption for the leaching.
	• Separation processes are simple.		• Fast leaching kinetics.
			• Inexpensive leaching agents.
			• Low energy consumption.
Disadvantages and H_2O_2 dosage	• High consumption of acids.		• 20% (v/v) H_2O_2 solution was employed to oxidize Fe(II) to Fe(III) after the leaching.
	• High consumption of energy for the leaching.		
	• Slow leaching kinetics.		
	• 10% (v/v) of H_2O_2 solution was employed as an oxidizing agent during leaching.		

of process as well as potential environmental impacts. However, in the case of leaching of the metallic alloys with ferric salt solutions, use of H_2O_2 to oxidize Fe(II) to Fe(III) in the leaching solution is necessary to separate iron by solvent extraction with D2EHPA. In hydrometallurgical process of zinc, iron is removed from the leaching solution of zinc calcine by precipitation as jarosite or goethite. Therefore, further work needs to be done to compare the separation efficiency of iron from the leaching solution between solvent extraction and precipitation.

4. Conclusions

Smelting reduction of spent LIBs at high temperature results in metallic alloys containing Cu, Co, Fe, Ni, and Mn. In order to develop a process to recover valuable metals from the metallic alloys, the use of either the mixture of ferric and ferrous ions or ferric ions as a leaching agent was investigated. Besides, the effect of leaching parameters such as iron salt concentration, reaction temperature and time, and pulp density on the leaching of the metals was investigated. The obtained results indicated that the mixture of $Fe_2(SO_4)_3$ and $FeSO_4$ and single $Fe_2(SO_4)_3$ or $FeCl_3$ solution can effectively dissolve the metals from the alloys with the same leaching ability at room temperature. The leaching of the metals from the alloys was ascribed to the reduction of ferric to ferrous ion and to the complex formation between the dissolved metal ions and the ligands. Optimum conditions for the complete leaching of metals were determined to be 0.35 mol/L $Fe_2(SO_4)_3$ or 0.7 mol/L $FeCl_3$, 12.5 g/L pulp density, 60 min at room temperature. Since iron exists as Fe(II) and Fe(III) in the leaching solution, 20% (v/v) H_2O_2 was added to the solution to oxidize Fe(II) to Fe(III). Three stage cross-current extraction of the solution with D2EHPA after oxidation of Fe(II) at an O/A ratio of unity led to complete extraction of Fe(III), while other metal ions such as Co(II), Cu(II), Mn(II), Ni(II) and Si(IV) remained in the raffinate. The Fe(III) loaded into D2EHPA was successfully stripped with 60% (v/v) aqua regia and the purity of Fe(III) in the stripping solution was higher than 99.9%. The remaining metal ions in the raffinate can be separated by applying our previously reported process.

The use of single ferric solutions for the leaching of metals from the alloys containing iron shows some advantages in the recovery of metals from the spent LIBs such as reduction in the dosage of acids and oxidizing agent, fast reaction rate, and low energy consumption. Considering these advantages, the application of ferric solutions to the leaching of metallic alloys from the spent LIBs can be a viable option.

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Author Contributions

Methodology and editing: Man Seung Lee; writing-original draft preparation: Thanh Tuan Tran. All authors have read and agreed to the published version of the manuscript.

Data availability

The data of this work could be obtained by contacting with the corresponding author by e-mail.

Declarations of competing interest

The authors declare no conflict of interest.

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UPOTREBA RASTVORA SOLI GVOŽĐA KAO AGENASA ZA LUŽENJE Co, Ni, Cu, Fe, i Mn IZ METALNIH LEGURA ISTROŠENIH LITIJUM-JONSKIH BATERIJA I SEPARACIJA GVOŽĐA IZ RASTVORA ZA LUŽENJE

T.T. Tran, M.S. Lee *

Odsek za nauku o naprednim materijalima i inženjerstvo, Institut za retke metale, Nacionalni univerzitet Mokpo, Čonam, Koreja

Apstrakt

Redukciono topljenje istrošenih litijum-jonskih baterija (LIB) dovodi do dobijanja metalnih legura koje sadrže Co, Ni, Cu, Fe i Mn. Da bi se dobili vredni metali sadržani u metalnim legurama, potrebno ih je rastvoriti. U ovom radu, kao sredstva za luženje korišćena je mešavina $Fe_2(SO_4)_3$ *i* $FeSO_4$*, pojedinačni rastvori* $Fe_2(SO_4)$ *i* $FeCl_3$*, i proučavani su uticaji parametara kao što su koncentracija soli gvožđa, temperatura i vreme reakcije i gustina pulpe na luženje metala. Razlika u procentu luženja metala zbog vrste rastvora gvožđa bila je beznačajna. U ovim sistemima za luženje, joni gvožđa i vodonika deluju kao oksidansi, a sulfatni/bisulfatni i hloridni anjoni deluju kao ligandi. Optimalni uslovi za potpuno ispiranje metala pojedinačnim rastvorima gvožđa bili su 0,35 mol/L* $Fe_2(SO_4)_3$ *ili 0,7 mol/L* $FeCl_3$ *pri gustini pulpe 12,5 g/L tokom 60 min na 22°C. Dodavanje* H_2O_2 *rastvoru za luženje za oksidaciju Fe(II) u Fe(III) poboljšalo je selektivnu ekstrakciju gvožđa preko Co(II), Ni(II), Cu(II), Mn(II) i Si (IV) pomoću D2EHPA. Uklanjanje gvožđa iz D2EHPA napunjenog sa carskom vodom rezultiralo je čistim rastvorom gvožđa. U poređenju sa rastvorima HCl i,* H_2SO_4*, upotreba jednog rastvora gvožđa pokazala je neke prednosti kao što su brza reakcija na 22°C i smanjenje doze kiselina i oksidanasa.*

Ključne reči: *Hidrometalurgija; Luženje; Recikliranje; Separacija; Litijum-jonske baterije*